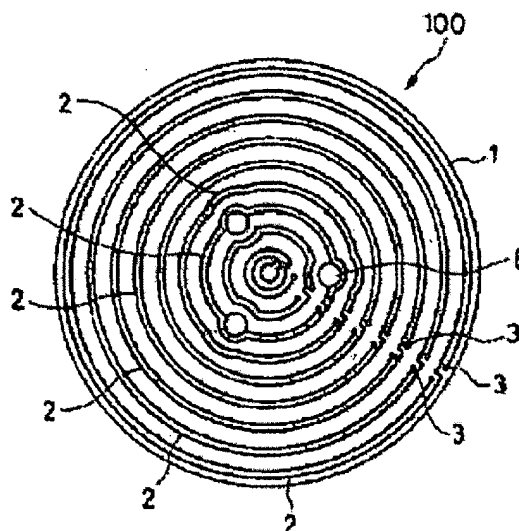


CONDUCTIVE PASTE FOR CERAMIC HEATER**Publication number:** JP2000323264**Publication date:** 2000-11-24**Inventor:** FURUKAWA MASAKAZU**Applicant:** IBIDEN CO LTD**Classification:****- international:** *H05B3/20; H01B1/22; H05B3/12; H05B3/20; H01B1/22; H05B3/12; (IPC1-7): H05B3/12; H01B1/22; H05B3/20***- European:****Application number:** JP20000106880 20000101**Priority number(s):** JP20000106880 20000101

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Abstract of JP2000323264

PROBLEM TO BE SOLVED: To improve adhesion with a ceramic substrate by including a metal and metal oxide in paste used for forming a heating element for a ceramic heater for drying. **SOLUTION:** Conductive paste including metal particles and metal oxide is printed relative to a ceramic plate 1. A heat generating element 2 is required to heat a heater 100 whole plate into a uniform temperature so as to be printed into a pattern formed of a concentric circle. The ceramic substrate 1 is heated and conductive paste is sintered so as to form the heat generating element 2 on the surface of the ceramic substrate 1. The conductive paste has resin and solvent removed by heating and sintering and at the same time the metal particles and the metal oxide sintered thereon. The temperature of the heating and sintering is set to 500-1000 deg.C. This conductive paste has the metal oxide included therein so that the metal particles and the ceramic substrate 1 are sintered and integrated under the presence of the metal oxide.



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(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開2000-323264

(P2000-323264A)

(43)公開日 平成12年11月24日(2000.11.24)

(51)Int.Cl. ⁷	識別記号	F I	ターミナル* (参考)
H 0 5 B 3/12		H 0 5 B 3/12	Λ
H 0 1 B 1/22		H 0 1 B 1/22	Λ
H 0 5 B 3/20	3 2 8	H 0 5 B 3/20	3 2 8

審査請求 有 請求項の数2 O L (全 5 頁)

(21)出願番号 特願2000-106880(P2000-106880)
(62)分割の表示 特願平9-210014の分割
(22)出願日 平成9年7月19日(1997.7.19)

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(54)【発明の名称】 セラミックヒーター用導電ペースト

(57)【要約】

【課題】 ヒーターとの密着性に優れた発熱体を形成するののに好都合な導電ペーストを提供すること。

【解決手段】 金属窒化物セラミックや金属耐火物セラミックからなるセラミック基板の発熱体形成用導電ペーストが、金属および金属酸化物を含むものである。

【特許請求の範囲】

【請求項1】 金属および金属酸化物を含有することを特徴とするセラミックヒーター用導電ペースト。

【請求項2】 金、銀、白金、パラジウム、鉛、タングステンおよびニッケルのうちから選ばれるいずれか1種以上からなる粒子と、酸化鉛、酸化亜鉛、酸化けい素、酸化ほう素、酸化アルミニウム、酸化イットリウムおよび酸化チタンのうちから選ばれるいずれか1種以上からなるものと、からなることを特徴とするセラミックヒーター用導電ペースト。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、主に半導体産業において使用される乾燥用セラミックヒーターの発熱体形成のために用いられる導電ペーストに関するものである。

【0002】

【従来の技術】半導体製品は、シリコンウエハー上に感光性樹脂をエッチングレジストとして形成し、そのシリコンウエハーをエッチングすることにより製造するのが普通である。その感光性樹脂は、シリコンウエハー表面にスピコートなどによって塗布されているが、塗布後は乾燥させなければならない。そのために、感光性樹脂を塗布したシリコンウエハーは、ヒーターを使って加熱する必要がある。従来、このようなヒーターとしては、金属（Al）板の裏面に、発熱体を配線したものが用いられている。

【0003】ところが、このような金属（Al）のヒーターは、次のような問題があった。それは、基板が金属製であるため、ヒーターの厚みは15mm程度と厚くしなければならぬことにある。なぜなら、薄い金属板では、加熱に起因する熱膨張により、反りや歪みが発生してしまい、金属板上に載置されるウエハーが破損したり、傾いたりするからである。そのため、ヒーターは重くなり、嵩張ってしまうという問題があった。しかも、このヒーターによる加熱温度は、発熱体への印加電圧や電流量を変えることにより制御しているが、金属板は厚いために、電圧や電流量の変化に対する応答性が悪く、温度が迅速に追従しないことから、温度制御しにくいという問題もあった。

【0004】

【発明が解決しようとする課題】これに対して最近、上記金属ヒーターのもつ問題点を克服するヒーターとして、セラミックヒーターが開発されている。このセラミックヒーターは温度制御しやすく、軽くて薄いという特長がある。しかしながら、セラミックヒーターは、ヒーター基板と発熱体との密着性が悪いという課題を抱えていた。本発明の目的は、セラミック基板との密着性に優れた発熱体を形成するための導電ペーストを提供することにある。

【0005】

【課題を解決するための手段】そこで発明者らは、セラミックヒーターの、とくに発熱体とヒーター基板との密着性について鋭意研究した結果、窒化物セラミックや炭化物セラミックの如きセラミック基板に対しては、金属粒子を含む導電ペーストの場合は本来、密着性が悪いのが普通であるが、この導電ペーストに金属酸化物を加えると、金属の粒子と窒化物セラミックや炭化物セラミックとがよく密着するようになることを知見した。

【0006】上記知見に基づいて構成された本発明は、金属および金属酸化物を含有することを特徴とするセラミックヒーター用導電ペーストである。なお、前記金属として、金、銀、白金、パラジウム、鉛、タングステンおよびニッケルのうちから選ばれるいずれか1種以上からなる粒子を用い、前記金属酸化物として、酸化鉛、酸化亜鉛、酸化けい素、酸化ほう素、酸化アルミニウム、酸化イットリウムおよび酸化チタンのうちから選ばれるいずれか1種以上からなるものを用いることが好ましい。

【0007】本発明を適用するときに用いられるセラミック基板（以下、単に「基板」という）は、窒化物セラミックまたは炭化物セラミックからなるものが用いられる。窒化物セラミックまたは炭化物セラミックは、熱膨張係数が金属より小さく、薄くしても、加熱により、反ったり歪んだりすることがない。そのため、ヒーター板を薄くて軽いものとすることができる。また、この基板は、熱伝導率が高く、また薄いため、その表面温度を発熱体の温度変化に迅速に追従させることができる。即ち、電圧や電流量を変えて発熱体の温度を変化させる際に、セラミック基板表面温度の制御が容易になる。かかる基板の厚さとしては、0.5～5mm程度がよい。薄すぎると破損しやすくなるからである。

【0008】なお、基板材である前記窒化物セラミックとしては、金属窒化物セラミック、例えば、窒化アルミニウム、窒化けい素、窒化ほう素および窒化チタンなどのうちから選ばれるいずれか1種以上のセラミックスが望ましい。また、炭化物セラミックとしては、金属炭化物セラミック、例えば、炭化けい素、炭化ジルコニウム、炭化チタン、炭化タンタル、炭化タングステンなどのうちから選ばれるいずれか1種以上のセラミックスが望ましい。これらのセラミックの中では、窒化アルミニウムが最も好適である。それは、窒化アルミニウムの場合、熱伝導率が180W/m・Kと最も高いからである。

【0009】本発明において、上記セラミック基板に設けられる発熱体は、導電ペースト、とくにその中の金属粒子および金属酸化物を焼結して形成される。即ち、かかる導電ペーストは、加熱焼成によってセラミック基板の表面に焼き付けることができる。この焼結時、金属粒子同士、金属粒子と基板セラミックとが融着する。こう

して得られた発熱体2は、図1に示すように、基板1全体の温度を均一にする必要があることから、同心円状のパターンがよい。また、発熱体2のパターンの厚さは、1~20 μ mが望ましく、幅は0.5~5mmが望ましい。厚さ、幅により抵抗値を変化させることができるが、この範囲が最も実用的だからである。抵抗値は、薄く、細くなるほど大きくなる。

【0010】本発明において、前記発熱体形成用導電ペーストは、金属（粒子）の他、樹脂、溶剤、増粘剤などを含むものが一般的である。その金属（粒子）としては、金、銀、白金、パラジウム、鉛、タングステン、ニッケルのうちから選ばれるいずれか1種以上のものがよい。これらの金属は、比較的酸化しにくく、発熱するのに十分な抵抗値を有するからである。これら金属は、粒径が0.1~100 μ mのものであることが望ましい。微細すぎると酸化しやすく、大きすぎると焼結しにくくなり、抵抗値が大きくなるからである。

【0011】かかる導電ペーストに使用される樹脂としては、エポキシ樹脂、フェノール樹脂などがよい。また、溶剤としては、イソプロピルアルコールなどが使用される。増粘剤としては、セルロースなどが挙げられる。

【0012】本発明にかかる前記導電ペーストの特徴は、前記金属粒子に加えて金属酸化物をも含むことにある。この理由は、窒化物セラミックまたは炭化物セラミックと金属粒子との密着性を改善するのに、金属酸化物が有効に作用するためである。即ち、金属酸化物を含有させることにより、窒化物セラミックまたは炭化物セラミックと、金属粒子との密着性がより一層改善されるからである。その理由は必ずしも明確ではないが、金属粒子表面および窒化物セラミックまたは炭化物セラミックの表面にはわずかに酸化膜が形成されており、この酸化膜同士が金属酸化物を介して一体化して焼結する結果、金属粒子と窒化物セラミックまたは炭化物セラミックとの密着性が向上するのではないかと推定される。

【0013】前記金属酸化物としては、酸化鉛、酸化亜鉛、酸化けい素（シリカ）、酸化ホウ素（ B_2O_3 ）、酸化アルミニウム（アルミナ）、酸化イットリウム（イットリア）、酸化チタン（チタニア）のうちから選ばれるいずれか1種以上がよい。これらの金属酸化物は、発熱体の抵抗値を大きくすることなく、金属粒子と窒化物セラミックまたは炭化物セラミックとの密着性を改善できるからである。

【0014】本発明にかかる上記導電ペーストを用いて発熱体を形成した場合、その発熱体の表面を金属層で被覆することが望ましい。発熱体は、金属粒子の焼結体であり、露出していると酸化しやすく抵抗値が変化してしまうからである。即ち、発熱体表面を金属層で被覆すると、酸化が防止できるからである。金属層の厚さとしては、0.1~10 μ m程度が望ましい。それは、発熱体の

抵抗値を変化させることなく、発熱体の酸化を防止できるからである。

【0015】発熱体の被覆に使用される金属は、非酸化性の金属であればよい。具体的には、金、銀、パラジウム、白金、ニッケルのうちから選ばれる少なくとも1種がよい。

【0016】なお、本発明において用いられる前記セラミック基板1は、図2に示すように、貫通孔8を複数設けてその孔8に支持ピン7を挿入し、そのピン7を介して発熱体2が設けられている側とは反対側に半導体ウエハー9を載置する。そして、支持ピン7を上下させて半導体ウエハー9を図示しない搬送機に渡したり、搬送機から半導体ウエハー9を受け取ったりすることができる。

【0017】次に、本発明にかかる導電ペーストを用いて発熱体およびセラミックヒーターそのものを製造する方法について以下に説明する。

(1) 窒化物セラミックまたは炭化物セラミックの粉体を焼結して窒化物セラミックまたは炭化物セラミックからなるセラミック基板を形成する工程。前述した窒化アルミニウムなどの窒化物セラミックまたは炭化けい素などの炭化物セラミックの粉体、必要に応じてイットリアなどの焼結助剤やバインダーなどをスプレードライなどの方法で顆粒状にし、この顆粒を金型などに入れて加圧し、板状に成形して生成形体を製造する。

【0018】このとき、生成形体に、必要に応じて半導体ウエハーの支持ピンを挿入する貫通孔や熱電対を埋め込む凹部を設けておく。次に、前記生成形体を加熱・焼成して焼結することにより、セラミック製板状の基板を製造する。加熱焼成の際は、加圧すれば気孔のないヒーターの製造に有効である。加熱焼成は、焼結温度以上であればよいが、窒化物セラミックまたは炭化物セラミックでは、1000~2500℃である。

【0019】(2) (1)のセラミック板に対し、金属粒子および金属酸化物を含む導電ペーストを印刷する工程。かかる導電ペーストとしては、上述した金属粒子、および上述した金属酸化物の他、さらに上述したような樹脂、溶剤からなる粘度の高い流動物が用いられる。この導電ペーストを、スクリーン印刷法などにより、セラミック基板の発熱体を設けようとする部分に印刷する。発熱体は、ヒーター板全体を均一な温度にする必要があることから、できれば図1に示すような同心円からなるパターンに印刷することが望ましい。

【0020】(3) 次に、前記セラミック基板を加熱して導電ペーストを焼結させ、セラミック基板の表面に発熱体を形成する工程。導電ペーストは、加熱焼成によって、樹脂や溶剤が除去されるとともに、金属粒子および金属酸化物が焼結される。このときの加熱焼成の温度は、500~1000℃である。この場合、本発明にかかる導電ペーストの場合、その中に金属酸化物を含有し

ているので、この金属酸化物の介在下に金属粒子およびセラミック基板とが焼結して一体化するため、発熱体とセラミック基板との密着性が向上する。

【0021】(4) さらに、前記発熱体の表面は金属層で被覆することが望ましい。被覆は、電解めっき、無電解めっき、スパッタリングにより行うことができるが、量産性を考慮すると無電解めっきが最適である。

【0022】(5) そして、前記発熱体のパターンの端部に、電源との接続のための端子を半田にて取り付けて製品のセラミックヒーターとする。

【0023】なお、取り付け部位には半田ペーストを印刷した後、端子を載せて200～500℃の温度に加熱するリフロー処理を行い、さらに、必要に応じて熱電対を埋め込んでもよい。以下、実施例に沿って説明する。

【0024】

【実施例】(実施例1) 窒化アルミニウムセラミック板

(1) 窒化アルミニウム粉末(平均粒径1.1 μm) 100重量部、イットリア(酸化イットリウムのこと 平均粒径0.4 μm) 4重量部、アクリルバイダー12重量部およびアルコールからなる組成物を、スプレードライヤー法にて顆粒状にした。

(2) 顆粒状粉末を金型にに入れて、平板状に成形して生成形体を得た。生成形体にドリル加工して、半導体ウエハー支持ピンを挿入する孔8、図示しないが、熱電対を埋め込むための凹部を設けた。

(3) 生成形体を、1800℃、圧力230 kg/cm^2 でホットプレスし、厚さ3mmの窒化アルミニウム板状体を得た。これを直径230mmの円状に切り出してセラミック製の板状体(セラミック基板)1とした。

【0025】(4) (3) で得たセラミック基板1に、スクリーン印刷にて導電ペーストを印刷した。印刷パターンは、図1に示すような同心円のパターンとした。導電ペーストは、徳力化学研究所製のソルベストPS603を使用した。この導電ペーストは、金属酸化物入り銀/鉛ペーストであり、金属酸化物として酸化鉛、酸化亜鉛、酸化けい素、酸化ほう素、酸化アルミニウムを含む。

(5) 上記導電ペーストを印刷したセラミック基板1を780℃で加熱焼成して、導電ペースト中の銀、鉛を焼結させるとともに、該基板1に焼き付けた。銀-鉛の焼結体4によるパターンは、厚さが5 μm 、幅2.4 mmであった。

【0026】(6) 硫酸ニッケル80 g/l 、次亜リン酸ナトリウム24 g/l 、酢酸ナトリウム12 g/l 、ホウ酸8 g/l 、塩化アンモニウム6 g/l の濃度の水溶液からなる無電解ニッケルめっき浴に、(5)のヒーター板を浸漬して、銀-鉛の焼結体4の表面に厚さ1 μm の

ニッケル層5を析出させて発熱体2とした。

(7) 電源との接続を確保するための端子を取付ける部分に、スクリーン印刷1より、銀-鉛半田ペーストを印刷して半田層(田中貴金属製)6を形成した。ついで、半田層6の上にコパール製の端子ピン3を載置して、420℃で加熱リフローし、端子ピン3を発熱体2の表面に取付けた。

(8) 温度制御のための熱電対(図示しない)を埋め込み、ヒーター100を得た。

【0027】(実施例2) 炭化けい素セラミック板
実施例1と基本的に同様であるが、平均粒径1.0 μm の炭化けい素粉末を使用し、焼結温度を1900℃とした。

【0028】実施例1、2のヒーターについて、電圧、電流量の変化に対する温度の追従性、発熱体のプル強度について測定した。ヒーターに電圧を印加したところ、実施例1のヒーターは0.5秒で温度変化が見られ、また、実施例2のヒーターは2秒で温度変化が観察された。発熱体2のプル強度については、実施例1のヒーターは3.1 kg/mm^2 、実施例2のヒーターは3 kg/mm^2 であった。

【0029】(比較例) アルミニウム板
発熱体としてシリコンゴムで挟持したニクロム線を用い、厚さ15mmのアルミニウム板とあて板で発熱体を挟み、ボルトで固定してヒーターとした。比較例のヒーターに電圧を印加したところ、温度変化が見られるまで24秒を要した。

【0030】

【発明の効果】以上説明したように、本発明によれば、セラミック基板と発熱体の密着性を向上させることができ、ひいては、薄くて軽いセラミックヒーターを提供することができ、実用的である。

【図面の簡単な説明】

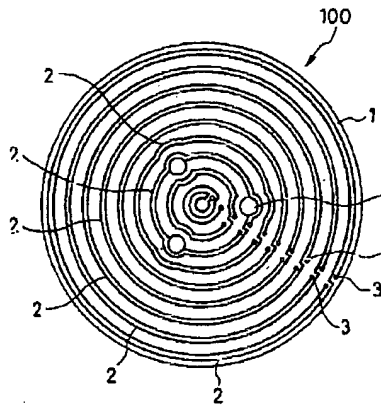
【図1】本発明にかかる導電ペーストを用いて形成した発熱体を有するセラミックヒーターの模式図。

【図2】ヒーターの使用状態を示す断面図。

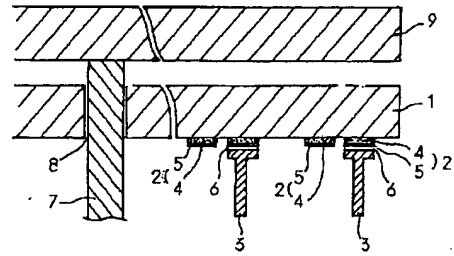
【符号の説明】

- 1 セラミック基板
- 2 発熱体
- 3 端子ピン
- 4 金属(銀-鉛)粒子焼結体
- 5 金属(ニッケル)被覆層
- 6 半田層
- 7 半導体ウエハー支持ピン
- 8 貫通孔
- 9 半導体製品
- 100 ヒーター

【図1】



【図2】



PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-323264

(43)Date of publication of application : 24.11.2000

(51)Int.Cl.

H05B 3/12

H01B 1/22

H05B 3/20

(21)Application number : 2000-106880

(71)Applicant : IBIDEN CO LTD

(22)Date of filing : 19.07.1997

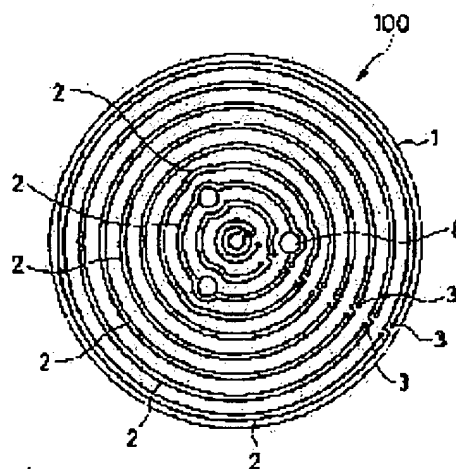
(72)Inventor : FURUKAWA MASAKAZU

(54) CONDUCTIVE PASTE FOR CERAMIC HEATER

(57)Abstract:

PROBLEM TO BE SOLVED: To improve adhesion with a ceramic substrate by including a metal and metal oxide in paste used for forming a heating element for a ceramic heater for drying.

SOLUTION: Conductive paste including metal particles and metal oxide is printed relative to a ceramic plate 1. A heat generating element 2 is required to heat a heater 100 whole plate into a uniform temperature so as to be printed into a pattern formed of a concentric circle. The ceramic substrate 1 is heated and conductive paste is sintered so as to form the heat generating element 2 on the surface of the ceramic substrate 1. The conductive paste has resin and solvent removed by heating and sintering and at the same time the metal particles and the metal oxide sintered thereon. The temperature of the heating and sintering is set to 500-1000°C. This conductive paste has the metal oxide included therein so that the metal particles and the ceramic substrate 1 are sintered and integrated under the presence of the metal oxide.



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CLAIMS

[Claim(s)]

[Claim 1]Conductive paste for ceramic heaters containing metal and a metallic oxide.

[Claim 2]Conductive paste for ceramic heaters characterized by comprising the following.

Particles which consist of any one or more sorts chosen from among gold, silver, platinum, palladium, lead, tungsten, and nickel.

What consists of any one or more sorts chosen from among lead oxide, a zinc oxide, an oxidation silicon, oxidation boron, an aluminum oxide, yttrium oxide, and titanium oxide

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The invention in this application relates to the conductive paste used for heating element formation of the ceramic heater for desiccation mainly used in semiconductor industry.

[0002]

[Description of the Prior Art]As for a semi conductor product, it is common to manufacture by forming a photopolymer as etching resist on a silicon wafer, and etching the silicon wafer. After spreading must be dried although the photopolymer is applied to the silicon wafer surface by the spin coater etc. Therefore, it is necessary to heat the silicon wafer which applied the photopolymer using a heater. Conventionally, as such a heater, it is metal. What wired the rear face of the (aluminum) board in the heating element is used.

[0003]However, such metal (aluminum) The heater had the following problems. Since a substrate is metal, if it is not thickened with about 15 mm and it is ****, it is, and the thickness of a heater is in things. It is because the wafer which curvature and distortion occur and is laid on a metal plate by the thermal expansion resulting from heating in a thin metal plate damages or inclines. Therefore, the heater became heavy and there was a problem of being bulky. And although the cooking temperature with this heater was controlled by changing the impressed electromotive force and the current amount to a heating element, since a metal plate was thick, the response to change of voltage or a current amount was bad, and there was also a problem of being hard to carry out temperature control, from temperature not following promptly.

[0004]

[Problem(s) to be Solved by the Invention]On the other hand, the ceramic heater is developed these days as a heater which conquers the problem which the above-mentioned metal heater has. It is easy to carry out temperature control of this ceramic heater, and there is the feature

that it is light and thin. However, the ceramic heater was holding the technical problem that the adhesion of a heater substrate and a heating element was bad. The purpose of this invention is to provide conductive paste for forming the heating element excellent in adhesion with a ceramic substrate.

[0005]

[Means for Solving the Problem] Then, as a result of [of a ceramic heater, artificers,] inquiring wholeheartedly about the adhesion of a heating element and a heater substrate especially, in the case of conductive paste which contains metal particles to a ceramic substrate like nitride ceramics or carbide ceramics, originally adhesion is usually bad but, and. When a metallic oxide was added to this conductive paste, the knowledge of particles, and metaled nitride ceramics and carbide ceramics coming to stick well was carried out.

[0006] This invention constituted based on the above-mentioned knowledge is conductive paste for ceramic heaters containing metal and a metallic oxide. Using particles which consist of any one or more sorts chosen from among gold, silver, platinum, palladium, lead, tungsten, and nickel as said metal, as said metallic oxide, It is preferred to use what consists of any one or more sorts chosen from among lead oxide, a zinc oxide, an oxidation silicon, oxidation boron, an aluminum oxide, yttrium oxide, and titanium oxide.

[0007] Ceramic substrate used when applying this invention (only henceforth a "substrate") What consists of nitride ceramics or carbide ceramics is used. Even if nitride ceramics or carbide ceramics have a coefficient of thermal expansion smaller than metal and it makes them thin, with heating, it curves or they are not distorted. Therefore, a heater plate can be made it is thin and light. Since this substrate is expensive and its thermal conductivity is thin, that skin temperature can be made to follow a temperature change of a heating element promptly. That is, when changing voltage and a current amount and changing temperature of a heating element, control of ceramic substrate skin temperature becomes easy. As thickness of this substrate, about 0.5-5 mm is good. It is because it will become easy to damage if too thin.

[0008] As said nitride ceramics which are substrate materials, any one or more sorts of ceramics chosen from among metal nitride ceramics, for example, alumimium nitride, a nitriding silicon, a boron nitride, titanium nitride, etc. are desirable. As carbide ceramics, any one or more sorts of ceramics chosen from among metallic carbide ceramics, for example, silicon carbide, zirconium carbide, titanium carbide, tantalum carbide, tungsten carbide, etc. are desirable. In these ceramics, alumimium nitride is the most preferred. In the case of alumimium nitride, that is because thermal conductivity is as the highest as 180 W/m-K.

[0009] In this invention, a heating element provided in the above-mentioned ceramic substrate sinters conductive paste especially metal particles in it, and a metallic oxide, and is formed. That is, this conductive paste can be printed on the surface of a ceramic substrate by heating calcination. Metal particles, metal particles, and substrate ceramics weld at the time of this

sintering. In this way, since the obtained heating element 2 needs to make temperature of the substrate 1 whole uniform as shown in drawing 1, its pattern of concentric circle shape is good. As for thickness of a pattern of the heating element 2, 1-20 micrometers is desirable, and 0.5-5 mm of width is desirable. Although resistance can be changed with thickness and width, it is because this range is the most practical. Resistance becomes so large that it becomes thinly and thin.

[0010]in this invention -- said conductive paste for heating element formation -- metal (particles) others -- a thing containing resin, a solvent, a thickener, etc. is common. The metal (particles) If it carries out, any one or more sorts of things chosen from among gold, silver, platinum, palladium, lead, tungsten, and nickel are good. It is because these metal cannot oxidize comparatively easily and it has sufficient resistance to generate heat. Particle diameter these metal It is desirable that it is what is 0.1-100 micrometers. It is because it will be easy to oxidize if too detailed, it will become difficult to sinter if too large, and resistance becomes large.

[0011]As resin used for this conductive paste, an epoxy resin, phenol resin, etc. are good. Isopropyl alcohol etc. are used as a solvent. Cellulose etc. are mentioned as a thickener.

[0012]There is the feature of said conductive paste concerning this invention in adding to said metal particles and a metallic oxide being included. This reason is for a metallic oxide to act effectively, although the adhesion of nitride ceramics or carbide ceramics, and metal particles is improved. That is, it is because the adhesion of nitride ceramics or carbide ceramics, and metal particles is improved further by making a metallic oxide contain. Although the reason is not necessarily clear, an oxide film is slightly formed in the surface of the metal-particles surface and nitride ceramics, or carbide ceramics, As a result of these oxide films' unifying and sintering via a metallic oxide, it is presumed whether adhesion with metal particles, nitride ceramics, or carbide ceramics improves.

[0013]as said metallic oxide -- lead oxide, a zinc oxide, and oxidation silicon (silica) . Boron oxide (B_2O_3) Aluminum oxide (alumina) Yttrium oxide (yttria) Titanium oxide (titania) Any one or more sorts chosen from inside are good. These metallic oxides are because adhesion with metal particles, nitride ceramics, or carbide ceramics is improvable, without enlarging resistance of a heating element.

[0014]When a heating element is formed using the above-mentioned conductive paste concerning this invention, it is desirable to cover the surface of the heating element with a metal layer. A heating element is a sintered compact of metal particles, and it is because resistance will change that it will be easy to oxidize if it has exposed. That is, it is because oxidation can be prevented if the heating element surface is covered with a metal layer. As thickness of a metal layer, about 0.1-10 micrometers is desirable. That is because oxidation of a heating element can be prevented, without changing resistance of a heating element.

[0015]The metal used for covering of a heating element should just be metal of a non-oxidizing quality. Specifically, at least one sort chosen from among gold, silver, palladium, platinum, and nickel is good.

[0016]As shown in drawing 2, said ceramic substrate 1 used in this invention forms two or more breakthroughs 8, inserts the holding pin 7 in the hole 8, and lays the semiconductor wafer 9 in an opposite hand with a side in which the heating element 2 is formed via the pin 7. And a conveyer which makes the holding pin 7 go up and down, and does not illustrate the semiconductor wafer 9 can be passed, or the semiconductor wafer 9 can be received from a conveyer.

[0017]Next, how to manufacture a heating element and the ceramic heater itself using conductive paste concerning this invention is explained below.

(1) A process of forming a ceramic substrate which sinters a granular material of nitride ceramics or carbide ceramics, and consists of nitride ceramics or carbide ceramics. A granular material of carbide ceramics, such as nitride ceramics, such as aluminium nitride mentioned above, or silicon carbide, Sintering aids, binders, etc., such as yttria, are made into granularity by methods, such as spray dry, if needed, this granulation is put into a metallic mold etc., and is pressurized, it fabricates to tabular, and a generation form is manufactured.

[0018]At this time, a crevice embedding a breakthrough which inserts a holding pin of a semiconductor wafer in a generation form if needed, or a thermo couple is provided. Next, a ceramic plate manufacturing-like board is manufactured by carrying out heating-calcination of said generation form, and sintering it. In the case of heating calcination, if it pressurizes, it is effective in manufacture of a heater without a stoma. Although the heating calcination should just be beyond sintering temperature, it is 1000-2500 ** in nitride ceramics or carbide ceramics.

[0019](2) A process of printing conductive paste containing metal particles and a metallic oxide to a ceramic plate of (1). A fluid with high viscosity which consists of resin which was further mentioned above and a solvent besides metal particles mentioned above and a metallic oxide mentioned above as this conductive paste is used. This conductive paste is printed with screen printing etc. into a portion which is going to provide a heating element of a ceramic substrate. As for a heating element, it is desirable to print to a pattern which consists of a concentric circle if it can do [be / necessary / to make the whole heater plate into a uniform temperature / it], as shown in drawing 1.

[0020](3) Next, a process of heating said ceramic substrate, making conductive paste sintering, and forming a heating element on the surface of a ceramic substrate. As for conductive paste, while resin and a solvent are removed by heating calcination, metal particles and a metallic oxide are sintered by it. Temperature of heating calcination at this time is 500-1000 **. In this case, since a metallic oxide is contained in it in the case of conductive paste

concerning this invention and metal particles and a ceramic substrate sinter and unify under an intervention of this metallic oxide, the adhesion of a heating element and a ceramic substrate improves.

[0021](4) As for the surface of said heating element, covering with a metal layer is still more desirable. Although electrolysis plating, nonelectrolytic plating, and sputtering can perform covering, nonelectrolytic plating is the optimal if mass production nature is taken into consideration.

[0022](5) And attach a terminal for connection with a power supply to an end of a pattern of said heating element with solder, and make it it with a ceramic heater of a product.

[0023]After printing soldering paste in an attachment part, reflow treatment which carries a terminal and is heated in temperature of 200-500 ** may be performed, and a thermo couple may also be embedded further if needed. Hereafter, it explains in accordance with an example.

[0024]

[Example](Example 1) Alumimium nitride ceramic plate (1) Aluminum nitride powder (mean-particle-diameter 1.1 μm) 100 weight sections, Yttria (yttrium oxide mean-particle-diameter 0.4 micrometer) The constituent which consists of four weight sections, acrylic Bayda' 12 weight section, and alcohol was made into granularity by the spray dryer method.

(2) Granular powder was put into the metallic mold, it fabricated to plate-like, and the generation form was acquired. Drilling was carried out to the generation form and the hole 8 which inserts a semiconductor wafer holding pin, and the crevice for embedding a thermo couple, although not illustrated were provided.

(3) The hotpress of the generation form was carried out by 1800 ** and pressure 230 kg/cm^2 , and the 3-mm-thick alumimium nitride plate was obtained. It is a diameter about this. It starts in round form of 230 mm, and is a plate made from ceramics. (ceramic substrate) It was referred to as 1.

[0025](4) To the ceramic substrate 1 obtained by (3), conductive paste was printed by screen-stencil. The printing pattern was used as the pattern of a concentric circle as shown in drawing 1. Tokuriki Chemical Research 603 [sorbet strike PS] was used for conductive paste. This conductive paste is silver containing a metallic oxide / lead paste.

Lead oxide, a zinc oxide, an oxidation silicon, oxidation boron, and an aluminum oxide are included as a metallic oxide.

(5) While carrying out heating calcination of the ceramic substrate 1 which printed the above-mentioned conductive paste by 780 ** and making the silver in conductive paste, and lead sinter, it printed on this substrate 1. The thickness of the pattern by the sintered compact 4 of silver-lead was 5 micrometers and width 2.4 mm.

[0026](6) 80 g/l of nickel sulfate, 24 g/l of sodium hypophosphite, It is (5) to the electroless nickel plating bath which consists of solution of the concentration of 12 g/l of sodium acetate, 8 g/l of boric acid, and 6 g/l of ammonium chloride. The heater plate was immersed, the 1-micrometer-thick nickel layer 5 was deposited on the surface of the sintered compact 4 of silver-lead, and it was considered as the heating element 2.

(7) Print silver-lead soldering paste from the screen-stencil 1 into the portion which attaches the terminal for securing connection with a power supply, and it is a solder layer. (product made from the Tanaka precious metals) 6 was formed. Subsequently, the terminal pin 3 made from covar was laid on the solder layer 6, a heating reflow was carried out by 420 **, and the terminal pin 3 was attached to the surface of the heating element 2.

(8) Thermo couple for temperature control (not shown) It embedded and the heater 100 was obtained.

[0027](Example 2) Although it was fundamentally [as the silicon carbide ceramic plate example 1] the same, the silicon carbide powder of mean-particle-diameter 1.0 μm was used, and sintering temperature was 1900 **.

[0028]It measured about the flattery nature [as opposed to / heater / of Examples 1 and 2 / change of voltage and a current amount] of temperature, and the pull intensity of the heating element. When voltage was impressed to the heater, the heater of Example 1 is 0.5. The temperature change was seen in the second and, as for the heater of Example 2, the temperature change was observed in 2 seconds. About the pull intensity of the heating element 2, the heater of 3.1 kg/mm^2 and Example 2 of the heater of Example 1 was 3 kg/mm^2 .

[0029](Comparative example) Using the Nichrome wire pinched by silicone rubber as an aluminum plate heating element, it hit with the 15-mm-thick aluminum plate, the heating element was pinched with the board, and it fixed with the bolt, and was considered as the heater. When voltage was impressed to the heater of a comparative example, 24 seconds was taken to see a temperature change.

[0030]

[Effect of the Invention]As explained above, according to this invention, the adhesion of a ceramic substrate and a heating element can be raised, a thin and light ceramic heater can be provided by extension, and it is practical.

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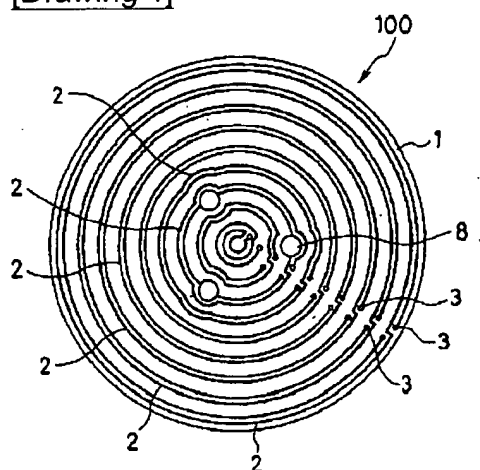
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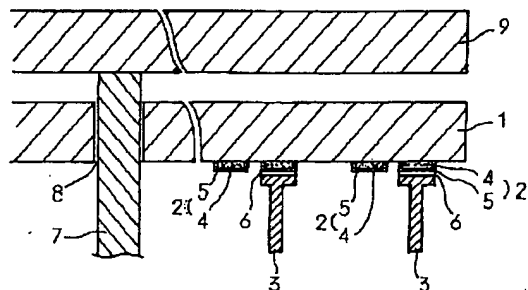
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DRAWINGS

[Drawing 1]



[Drawing 2]



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CORRECTION OR AMENDMENT

[Kind of official gazette]Printing of amendment by regulation of 2 of Article 17 of Patent Law
[Section classification] The 1st classification of the part VII gate
[Publication date]November 30 (2001.11.30), Heisei 13

[Publication No.]JP,2000-323264,A (P2000-323264A)
[Date of Publication]November 24, Heisei 12 (2000.11.24)
[Annual volume number] Publication of patent applications 12-3233
[Application number]Application for patent 2000-106880 (P2000-106880)
[The 7th edition of International Patent Classification]

H05B 3/12

H01B 1/22

H05B 3/20 328

[FI]

H05B 3/12 A

H01B 1/22 A

H05B 3/20 328

[Written amendment]

[Filing date]May 8, Heisei 13 (2001.5.8)

[Amendment 1]

[Document to be Amended]Specification

[Item(s) to be Amended]Whole sentence

[Method of Amendment]Change

[Proposed Amendment]

[Document Name]Specification

[Title of the Invention]Conductive paste for ceramic heaters, and a ceramic heater

[Claim(s)]

[Claim 1]Conductive paste for ceramic heaters containing metal and a metallic oxide.

[Claim 2]Conductive paste for ceramic heaters characterized by comprising the following.

Particles which consist of any one or more sorts chosen from among gold, silver, platinum, palladium, lead, tungsten, and nickel.

What consists of any one or more sorts chosen from among lead oxide, a zinc oxide, an oxidation silicon, oxidation boron, an aluminum oxide, yttrium oxide, and titanium oxide

[Claim 3]A ceramic heater characterized by coming to form a heating element containing metal and a metallic oxide in a field of an opposite hand with a side in which a semiconductor wafer is located among the surfaces of a ceramic substrate which consists of nitride ceramics or carbide ceramics.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The invention in this application relates to the conductive paste used for heating element formation of the ceramic heater for desiccation mainly used in semiconductor industry, and a ceramic heater.

[0002]

[Description of the Prior Art]As for a semi conductor product, it is common to manufacture by forming a photopolymer as etching resist on a silicon wafer, and etching the silicon wafer. After spreading must be dried although the photopolymer is applied to the silicon wafer surface by the spin coater etc. Therefore, it is necessary to heat the silicon wafer which applied the photopolymer using a heater. Conventionally, as such a heater, it is metal. (aluminum) What wired the rear face of the board in the heating element is used.

[0003]However, such metal (aluminum) The heater had the following problems. Since a substrate is metal, if it is not thickened with about 15 mm and it is ****, it is, and the thickness of a heater is in things. It is because the wafer which curvature and distortion occur and is laid on a metal plate by the thermal expansion resulting from heating in a thin metal plate damages or inclines. Therefore, the heater became heavy and there was a problem of being bulky. And although the cooking temperature with this heater was controlled by changing the impressed electromotive force and the current amount to a heating element, since a metal plate was thick, the response to change of voltage or a current amount was bad, and there was also a problem of being hard to carry out temperature control, from temperature not following promptly.

[0004]

[Problem(s) to be Solved by the Invention]On the other hand, the ceramic heater is developed these days as a heater which conquers the problem which the above-mentioned metal heater has. It is easy to carry out temperature control of this ceramic heater, and there is the feature that it is light and thin. However, the ceramic heater was holding the technical problem that the adhesion of a heater substrate and a heating element was bad. The purpose of this invention is to provide conductive paste for forming the heating element excellent in adhesion with a ceramic substrate, and the ceramic heater heater which forms a heating element using this conductive paste.

[0005]

[Means for Solving the Problem]Then, as a result of [of a ceramic heater, artificers,] inquiring wholeheartedly about the adhesion of a heating element and a heater substrate especially, in the case of conductive paste which contains metal particles to a ceramic substrate like nitride ceramics or carbide ceramics, originally adhesion is usually bad but, and. When a metallic oxide was added to this conductive paste, the knowledge of particles, and metaled nitride ceramics and carbide ceramics coming to stick well was carried out.

[0006]The 1st thing of this invention constituted based on the above-mentioned knowledge is conductive paste for ceramic heaters containing metal and a metallic oxide. Using particles which consist of any one or more sorts chosen from among gold, silver, platinum, palladium, lead, tungsten, and nickel as said metal, as said metallic oxide, It is preferred to use what consists of any one or more sorts chosen from among lead oxide, a zinc oxide, an oxidation silicon, oxidation boron, an aluminum oxide, yttrium oxide, and titanium oxide.

[0007]Inside of the surface of a ceramic substrate where the 2nd thing of this invention consists of nitride ceramics or carbide ceramics, A side in which a semiconductor wafer is located is a ceramic heater characterized by coming to form in a field of an opposite hand a heating element which printed conductive paste containing metal and a metallic oxide, and which is produced by carrying out back heating calcination.

[0008]Ceramic substrate used when applying this invention (only henceforth a "substrate") What consists of nitride ceramics or carbide ceramics is used. Even if nitride ceramics or carbide ceramics have a coefficient of thermal expansion smaller than metal and it makes them thin, with heating, it curves or they are not distorted. Therefore, a heater plate can be made it is thin and light. Since this substrate is expensive and its thermal conductivity is thin, that skin temperature can be made to follow a temperature change of a heating element promptly. That is, when changing voltage and a current amount and changing temperature of a heating element, control of ceramic substrate skin temperature becomes easy. As thickness of this substrate, about 0.5-5 mm is good. It is because it will become easy to damage if too thin.

[0009]As said nitride ceramics which are substrate materials, any one or more sorts of ceramics chosen from among metal nitride ceramics, for example, alumimium nitride, a

nitriding silicon, a boron nitride, titanium nitride, etc. are desirable. As carbide ceramics, any one or more sorts of ceramics chosen from among metallic carbide ceramics, for example, silicon carbide, zirconium carbide, titanium carbide, tantalum carbide, tungsten carbide, etc. are desirable. In these ceramics, aluminum nitride is the most preferred. In the case of aluminum nitride, that is because thermal conductivity is as the highest as 180 W/m-K.

[0010]In this invention, a heating element provided in the above-mentioned ceramic substrate sinters conductive paste especially metal particles in it, and a metallic oxide, and is formed. That is, this conductive paste can be printed on the surface of a ceramic substrate by heating calcination. Metal particles, metal particles, and substrate ceramics weld at the time of this sintering. In this way, since the obtained heating element 2 needs to make temperature of the substrate 1 whole uniform as shown in drawing 1, its pattern of concentric circle shape is good. As for thickness of a pattern of the heating element 2, 1-20 micrometers is desirable, and 0.5-5 mm of width is desirable. Although resistance can be changed with thickness and width, it is because this range is the most practical. Resistance becomes so large that it becomes thinly and thin.

[0011]in this invention -- said conductive paste for heating element formation -- metal (particles) others -- a thing containing resin, a solvent, a thickener, etc. is common. The metal (particles) If it carries out, any one or more sorts of things chosen from among gold, silver, platinum, palladium, lead, tungsten, and nickel are good. It is because these metal cannot oxidize comparatively easily and it has sufficient resistance to generate heat. Particle diameter these metal It is desirable that it is what is 0.1-100 micrometers. It is because it will be easy to oxidize if too detailed, it will become difficult to sinter if too large, and resistance becomes large.

[0012]As resin used for this conductive paste, an epoxy resin, phenol resin, etc. are good. Isopropyl alcohol etc. are used as a solvent. Cellulose etc. are mentioned as a thickener.

[0013]There is the feature of said conductive paste concerning this invention in adding to said metal particles and a metallic oxide being included. This reason is for a metallic oxide to act effectively, although the adhesion of nitride ceramics or carbide ceramics, and metal particles is improved. That is, it is because the adhesion of nitride ceramics or carbide ceramics, and metal particles is improved further by making a metallic oxide contain. Although the reason is not necessarily clear, an oxide film is slightly formed in the surface of the metal-particles surface and nitride ceramics, or carbide ceramics, As a result of these oxide films' unifying and sintering via a metallic oxide, it is presumed whether adhesion with metal particles, nitride ceramics, or carbide ceramics improves.

[0014]as said metallic oxide -- lead oxide, a zinc oxide, and oxidation silicon (silica) . Boron oxide (B_2O_3) Aluminum oxide (alumina) Yttrium oxide (yttria) Titanium oxide (titania) Any one or more sorts chosen from inside are good. These metallic oxides are because adhesion with

metal particles, nitride ceramics, or carbide ceramics is improvable, without enlarging resistance of a heating element.

[0015]When a heating element is formed using the above-mentioned conductive paste concerning this invention, it is desirable to cover the surface of the heating element with a metal layer. A heating element is a sintered compact of metal particles, and it is because resistance will change that it will be easy to oxidize if it has exposed. That is, it is because oxidation can be prevented if the heating element surface is covered with a metal layer. As thickness of a metal layer, about 0.1-10 micrometers is desirable. That is because oxidation of a heating element can be prevented, without changing resistance of a heating element.

[0016]The metal used for covering of a heating element should just be metal of a non-oxidizing quality. Specifically, at least one sort chosen from among gold, silver, palladium, platinum, and nickel is good.

[0017]As shown in drawing 2, said ceramic substrate 1 used in this invention forms two or more breakthroughs 8, inserts the holding pin 7 in the hole 8, and lays the semiconductor wafer 9 in an opposite hand with a side in which the heating element 2 is formed via the pin 7. And a conveyer which makes the holding pin 7 go up and down, and does not illustrate the semiconductor wafer 9 can be passed, or the semiconductor wafer 9 can be received from a conveyer.

[0018]Next, how to manufacture a heating element and the ceramic heater itself using conductive paste concerning this invention is explained below.

(1) A process of forming a ceramic substrate which sinters a granular material of nitride ceramics or carbide ceramics, and consists of nitride ceramics or carbide ceramics. A granular material of carbide ceramics, such as nitride ceramics, such as alumimium nitride mentioned above, or silicon carbide, Sintering aids, binders, etc., such as yttria, are made into granularity by methods, such as spray dry, if needed, this granulation is put into a metallic mold etc., and is pressurized, it fabricates to tabular, and a generation form is manufactured.

[0019]At this time, a crevice embedding a breakthrough which inserts a holding pin of a semiconductor wafer in a generation form if needed, or a thermo couple is provided. Next, a ceramic plate manufacturing-like board is manufactured by carrying out heating-calcination of said generation form, and sintering it. In the case of heating calcination, if it pressurizes, it is effective in manufacture of a heater without a stoma. Although the heating calcination should just be beyond sintering temperature, it is 1000-2500 ** in nitride ceramics or carbide ceramics.

[0020](2) A process of printing conductive paste containing metal particles and a metallic oxide to a ceramic plate of (1). A fluid with high viscosity which consists of resin which was further mentioned above and a solvent besides metal particles mentioned above and a metallic oxide mentioned above as this conductive paste is used. This conductive paste is printed with screen

printing etc. into a portion which is going to provide a heating element of a ceramic substrate. As for a heating element, it is desirable to print to a pattern which consists of a concentric circle if it can do [be / necessary / to make the whole heater plate into a uniform temperature / it], as shown in drawing 1.

[0021](3) Next, a process of heating said ceramic substrate, making conductive paste sintering, and forming a heating element on the surface of a ceramic substrate. As for conductive paste, while resin and a solvent are removed by heating calcination, metal particles and a metallic oxide are sintered by it. Temperature of heating calcination at this time is 500-1000 **. In this case, since a metallic oxide is contained in it in the case of conductive paste concerning this invention and metal particles and a ceramic substrate sinter and unify under an intervention of this metallic oxide, the adhesion of a heating element and a ceramic substrate improves.

[0022](4) As for the surface of said heating element, covering with a metal layer is still more desirable. Although electrolysis plating, nonelectrolytic plating, and sputtering can perform covering, nonelectrolytic plating is the optimal if mass production nature is taken into consideration. Thus, inside of the surface of a ceramic substrate which consists of nitride ceramics or carbide ceramics, A ceramic heater characterized by coming to form in it a heating element produced by carrying out heating calcination after printing conductive paste containing metal and a metallic oxide to a field of an opposite hand with a side in which a semiconductor wafer is located is obtained.

[0023](5) And attach a terminal for connection with a power supply to an end of a pattern of said heating element with solder, and make it it with a ceramic heater of a product.

[0024]After printing soldering paste in an attachment part, reflow treatment which carries a terminal and is heated in temperature of 200-500 ** may be performed, and a thermo couple may also be embedded further if needed. Hereafter, it explains in accordance with an example.

[0025]

[Example](Example 1) Alumimium nitride ceramic plate

(1) Aluminum nitride powder (mean-particle-diameter 1.1 μm) 100 A weight section, yttria (yttrium oxide mean-particle-diameter 0.4 micrometer) The constituent which consists of four weight sections, acrylic Bayda' 12 weight section, and alcohol was made into granularity by the spray dryer method. (2) Granular powder was put into the metallic mold, it fabricated to plate-like, and the generation form was acquired. Drilling was carried out to the generation form and the hole 8 which inserts a semiconductor wafer holding pin, and the crevice for embedding a thermo couple, although not illustrated were provided.

(3) The hotpress of the generation form was carried out by 1800 ** and pressure 230 kg/cm^2 , and the 3-mm-thick alumimium nitride plate was obtained. It is a diameter about this. It starts in

round form of 230 mm, and is a plate made from ceramics. (ceramic substrate) It was referred to as 1.

[0026](4) To the ceramic substrate 1 obtained by (3), conductive paste was printed by screen-stencil. The printing pattern was used as the pattern of a concentric circle as shown in drawing 1. Tokuriki Chemical Research 603 [sorbet strike PS] was used for conductive paste. This conductive paste is silver containing a metallic oxide / lead paste.

Lead oxide, a zinc oxide, an oxidation silicon, oxidation boron, and an aluminum oxide are included as a metallic oxide.

(5) While carrying out heating calcination of the ceramic substrate 1 which printed the above-mentioned conductive paste by 780 ** and making the silver in conductive paste, and lead sinter, it printed on this substrate 1. The thickness of the pattern by the sintered compact 4 of silver-lead was 5 micrometers and width 2.4 mm.

[0027](6) 80 g/l of nickel sulfate, 24 g/l of sodium hypophosphite, It is (5) to the electroless nickel plating bath which consists of solution of the concentration of 12 g/l of sodium acetate, 8 g/l of boric acid, and 6 g/l of ammonium chloride. The heater plate was immersed, the 1-micrometer-thick nickel layer 5 was deposited on the surface of the sintered compact 4 of silver-lead, and it was considered as the heating element 2.

(7) Print silver-lead soldering paste from the screen-stencil 1 into the portion which attaches the terminal for securing connection with a power supply, and it is a solder layer. (product made from the Tanaka precious metals) 6 was formed. Subsequently, the terminal pin 3 made from covar was laid on the solder layer 6, a heating reflow was carried out by 420 **, and the terminal pin 3 was attached to the surface of the heating element 2.

(8) Thermo couple for temperature control (not shown) It embedded and the heater 100 was obtained.

[0028](Example 2) Silicon carbide ceramic plate

Although it was fundamentally [as Example 1] the same, the silicon carbide powder of mean-particle-diameter 1.0 μm was used, and sintering temperature was 1900 **.

[0029]It measured about the flattery nature [as opposed to / heater / of Examples 1 and 2 / change of voltage and a current amount] of temperature, and the pull intensity of the heating element. When voltage was impressed to the heater, the heater of Example 1 is 0.5. The temperature change was seen in the second and, as for the heater of Example 2, the temperature change was observed in 2 seconds. About the pull intensity of the heating element 2, the heater of 3.1 kg/mm^2 and Example 2 of the heater of Example 1 was 3 kg/mm^2 2.

[0030](Comparative example) Aluminum plate

Using the Nichrome wire pinched by silicone rubber as a heating element, it hit with the 15-

mm-thick aluminum plate, the heating element was pinched with the board, and it fixed with the bolt, and was considered as the heater. When voltage was impressed to the heater of a comparative example, 24 seconds was taken to see a temperature change.

[0031]

[Effect of the Invention]As explained above, according to this invention, the adhesion of a ceramic substrate and a heating element can be raised, a thin and light ceramic heater can be provided by extension, and it is practical.

[Brief Description of the Drawings]

[Drawing 1]The mimetic diagram of a ceramic heater which has the heating element formed using conductive paste concerning this invention.

[Drawing 2]The sectional view showing the condition of use of a heater.

[Description of Notations]

- 1 Ceramic substrate
- 2 Heating element
- 3 Terminal pin
- 4 Metal (silver-lead) Particle sintered compact
- 5 Metal (nickel) Enveloping layer
- 6 Solder layer
- 7 Semiconductor wafer holding pin
- 8 Breakthrough
- 9 Semi conductor product
- 100 Heater

[Translation done.]